CHEMICAL SPECIATION OF Hg(II) WITH ENVIRONMENTAL INORGANIC LIGANDS

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BACKGROUND

Complex formation between Hg(II) and the common environmental ligands Cl^-, OH^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-} can have profound effects on Hg(II) speciation in natural waters with low concentrations of organic matter. Hg(II) is labile, so its distribution amongst these inorganic ligands can be estimated by numerical modelling if reliable values for the relevant stability constants are available. This poster summarises the results of a critical review of such constants and related thermodynamic data.

It also forms part of a much larger project (covering Hg^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}), commissioned by IUPAC.

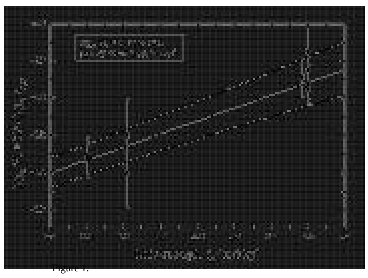

Figure 1.

Recommended values for the Hg^{2+} - OH^- - Cl^- system at 25 °C and I = 0.

Reaction	$\log_{10} ß^0$	? e/kg mol^{-1}
$Hg^{2+} + H_2O$? $HgOH^+ + H^+$	-3.40 ± 0.08	-0.14 ± 0.03
$Hg^{2+} + 2H_2O$? $Hg(OH)_2 + 2H^+$	-5.98 ± 0.06	-0.14 ± 0.03
$Hg^{2+} + 3H_2O$? $Hg(OH)_3^- + 3H^+$	-20.8 ± 0.06	-
$HgO(s) + 2H^+$? $Hg^{2+} + H_2O$ (*K_{s0})	2.37 ± 0.08	
$Hg^{2+} + Cl^-$? $HgCl^+$	7.31 ± 0.04	-0.22 ± 0.04
$Hg^{2+} + 2Cl^-$? $HgCl_2$	14.00 ± 0.07	-0.39 ± 0.03
$HgCl_2 + Cl^-$? $HgCl_3^-$	0.92 ± 0.09	0.01 ± 0.05
$HgCl_3^- + Cl^-$? $HgCl_4^-$	0.61 ± 0.12	0.00 ± 0.06
$Hg^{2+} + Cl^- + H_2O$? $HgOHCl + H^+$	4.27 ± 0.35	-0.24 ± 0.10

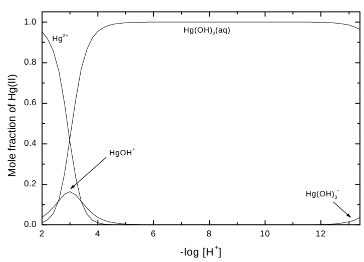

Figure 2. **Speciation diagram for the Hg^{2+} - OH^- system** at I = 0 mol kg^{-1}, applicable for $[Hg(II)]_T$ < *ca.* 10^{-5} mol L^{-1}. Results outside the –log [H$^+$] range of 2 to 12 should be viewed with caution as activity coefficients deviate from 1.0.

SIT – The Specific Ion Interaction Theory

For the general reaction (omitting most charges for simplicity):

$$pM + qL + rH_2O \; ? \; M_pL_q(OH)_r + rH^+ \quad (1)$$

the formation constant $b_{p,q,r}$ determined in a medium NX at finite I (molality) is related to that at I = 0, $ß_{p,q,r}°$, by:

$$\log_{10} b_{p,q,r} = \log_{10} b_{p,q,r}° + p\log_{10} g(M) + q\log_{10} g(L) + r\log_{10} a(H_2O) - \log_{10} g_{p,q,r} - r\log_{10} g(H^+) \quad (2)$$

where $g_{p,q,r}$ refers to the species $M_pL_q(OH)_r$.

With $\log_{10} g_i = -z_i^2 A\text{Ö} I (1 + 1.5\text{Ö} I)^{-1} + \Sigma_k e(i,k) m_k = -z_i^2 D + \Sigma_k e(i,k) m_k$

one obtains

$$\log_{10} b_{p,q,r} - \Delta z^2 D - r\log_{10} a(H_2O) = \log_{10} b_{p,q,r}° - \Delta e I \quad (3)$$

where $\Delta z^2 = (pz_M + qz_L - r)^2 + r - p(z_M)^2 - q(z_L)^2$

and $\Delta e = e(\text{complex N}^+ \text{ or X}^-) + re(H^+, X^-) - pe(M^+, X^-) - qe(L^-, N^+)$

The application of SIT to reliable literature values involved regression of $\log_{10} b_{p,q,r} - \Delta z^2 D - r\log_{10} a(H_2O)$, using equation (3). The intercept at I_m = 0 mol kg^{-1} gives $\log_{10} b_{p,q,r}°$. This is shown in Figure 1 for reaction (4) for which Δz^2 = −2 and r = 1.

$$Hg^{2+} + H_2O \; ? \; HgOH^+ + H^+ \quad (4)$$

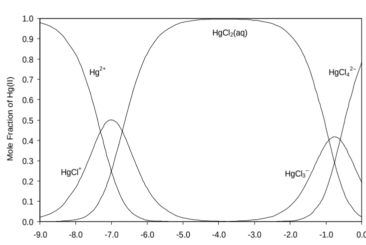

Figure 3. **Hg(II) - Cl^- speciation diagram** at 25 °C and I = 0. Hydrolysis is suppressed. Results for log [Cl^-] > -2.0 should be viewed with caution as activity coefficients deviate from 1.0

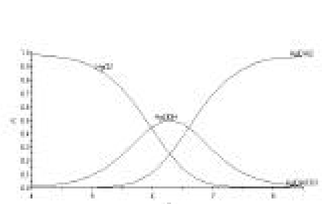

Figure 4. **Speciation diagram for the Hg^{2+} - H^+ - Cl^- - CO_2 - HPO_4^{2-} - SO_4^{2-} system** with $[Cl^-]_T$ = 0.23 mM, $[SO_4^{2-}]_T$ = 0.42 mM, $[HPO_4^{2-}]_T$ = 0.7 µM and $[Hg(II)]_T$ = 1 nM. Equilibrium with air having a CO_2 fugacity of 370 µbar.

REFERENCES

- Kipton J. Powell et al. *Pure and Applied Chem.* Vol. 77, No 4, pp 739-800, 2005
- Kipton J. Powell et al. *Aust. J. Chem*. 57, pp 993-1000, 2004

CONCLUSION

Under typical environmental conditions the predominating Hg(II) species are $HgCl_2(aq)$, $HgClOH(aq)$ and $Hg(OH)_2(aq)$.